A2

3/5/1
DIALOG(R)File 351:Derwent WPI

010138614 **Image available**
WPI Acc No: 1995-039865/ **199506**
Related WPI Acc No: 1994-138676; 1994-194696; 1994-194708; 1994-258103; 1994-361121; 1995-002302; 1995-002332; 1995-039866; 1995-039867; 1996-323607
XRAM Acc No: C95-017587
XRPX Acc No: N95-031579

Electrode for non-aqueous electrolyte batteries - uses lithium and powder of metal compound having many polycrystal objects consisting end of super particle placed along its grain boundary or inside

Patent Assignee: NIPPONDENSO CO LTD (NPDE)
Inventor: HASEGAWA ; ISOYAMA H; KOJIMA H; SAITO H; SUZUKI S
Number of Countries: 002 Number of Patents: 002
Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week	
JP 6236756	A	19940823	JP 9395593	A	19930329	199506	B
US 5494762	A	19960227	US 93114226	A	19930901	199614	
			US 95386363	A	19950209		

Priority Applications (No Type Date): JP 92353675 A 19921214; JP 92233841 A 19920901; JP 92233849 A 19920901; JP 92233857 A 19920901; JP 92304786 A 19921016; JP 92353672 A 19921214; JP 92353673 A 19921214; JP 92334673 A 19921215; JP 9395591 A 19930329; JP 9395592 A 19930329; JP 9395594 A 19930329; JP 9396799 A 19930330; JP 9396800 A 19930330; JP 9398973 A 19930331
Patent Details:

Patent No	Kind	Lan	Pg	Main IPC	Filing Notes
JP 6236756	A		4	H01M-004/48	
US 5494762	A		64	H01M-006/14	Cont of application US 93114226
					patent JP 6084512
					patent JP 6132027
					patent JP 6132040
					patent JP 6187994
					patent JP 6236756
					patent JP 6236757
					patent JP 6236758
					patent JP 6283153
					patent JP 6290773
					patent JP 6290814

Abstract (Basic): JP 6236756 A

Electrode for non-aqueous electrolyte batteries uses lithium as the electrode active material and a powder of metal cpd. (9) is emitted. The powder of a metal compound is made up of many polycrystal object particles (3) having an end (1) of a superparticle. The end of the superparticle exists along the boundary of the polycrystal object particle or inside it. The end of a superparticle does not react with the polycrystal object particles.

ADVANTAGE - Controls decay of particle of electrode active material. Increases life time of electrode for non-aqueous electrolyte batteries.

Dwg.1/4

Title Terms: ELECTRODE; NON; AQUEOUS; ELECTROLYTIC; BATTERY; LITHIUM; POWDER; METAL; COMPOUND; POLYCRYSTALLINE; OBJECT; CONSIST; END; SUPER; PARTICLE; PLACE; GRAIN; BOUNDARY
Derwent Class: A85; L03; M22; U24; X16
International Patent Class (Main): H01M-004/48; H01M-006/14
International Patent Class (Additional): H01M-010/40
File Segment: CPI; EPI

A2

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報**（Ａ）　(11)特許出願公開番号

特開平6－236756

(43)公開日　平成６年(1994) ８月23日

(51)Int.Cl.⁵	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｈ０１Ｍ　4/48				

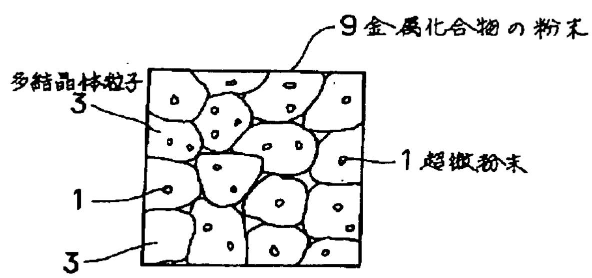
審査請求　未請求　請求項の数２　ＦＤ　（全 ４ 頁）

(21)出願番号	特願平5－95593
(22)出願日	平成５年(1993) ３月29日
(31)優先権主張番号	特願平4－353675
(32)優先日	平４(1992)12月14日
(33)優先権主張国	日本（ＪＰ）

(71)出願人　000004260
日本電装株式会社
愛知県刈谷市昭和町１丁目１番地
(72)発明者　鈴木　覚
愛知県刈谷市昭和町１丁目１番地　日本電装株式会社内
(72)発明者　長谷川　順
愛知県刈谷市昭和町１丁目１番地　日本電装株式会社内
(72)発明者　斉藤　博彦
愛知県刈谷市昭和町１丁目１番地　日本電装株式会社内
(74)代理人　弁理士　高橋　祥泰

(54)【発明の名称】　非水電解質電池用電極

(57)【要約】
【目的】　充放電に伴う電極活物質の微粉化や結晶構造の崩壊を抑制し，充放電サイクル寿命の長い非水電解質電池用電極を提供すること。
【構成】　リチウムを吸蔵，放出しうる金属化合物の粉末９を，電極活物質として用いた非水電解質電池用電極である。金属化合物の粉末９は，多結晶体粒子３の集合体からなると共に超微粉末１を含有している。超微粉末１は，多結晶体粒子３の粒子内或いは結晶粒界もしくはその両方に存在している。超微粉末１は，多結晶体粒子３と反応しないものである。超微粉末１の粒径は３μm以下が好ましい。リチウムを吸蔵，放出しうる金属化合物は，リチウムを含む金属化合物であることが好ましい。



【特許請求の範囲】

【請求項１】　リチウムを吸蔵，放出しうる金属化合物の粉末を電極活物質として用いた非水電解質電池用電極であって，上記金属化合物の粉末は多結晶体粒子の集合体からなると共に超微粉末を含有し，該超微粉末は，上記多結晶体粒子の粒子内或いは結晶粒界もしくはその両方に存在していることを特徴とする非水電解質電池用電極。

【請求項２】　請求項１において，上記リチウムを吸蔵，放出しうる金属化合物は，リチウムを含む金属化合物であることを特徴とする非水電解質電池用電極。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は，充放電に伴う電極活物質の微粉化や結晶構造の崩壊を抑制し，充放電サイクル寿命の長い非水電解質電池用電極に関する。

【０００２】

【従来技術】リチウム又はリチウム合金を電極とする非水電解質二次電池においては，その電極活物質として，従来より，MnO_2，V_2O_5 等の金属化合物が検討されている。しかし，これらの金属酸化物は，充放電による結晶構造の破壊のためエネルギ容量の減少が著しい。その対策として，予めリチウムイオンを含んだ$LiMn_2O_4$ 等のリチウム複合酸化物を，金属化合物として用いることが提案されている（Ｍａｔｅｒｉａｌ　Ｒｅｓｅａｒｃｈ　Ｂｕｌｌｅｔｉｎ　１８（１９８３）４６１－４７２）。

【０００３】図３に示すごとく，$LiMn_2O_4$ からなる金属化合物の粉末９は，多結晶体粒子３の集合体である。該多結晶体粒子３は，スピネル構造をした立方晶の結晶構造である。この金属化合物の粉末９の粒径は一般に数μｍから数十μｍである。上記金属化合物の粉末は，例えば，リチウム塩粉末とマンガン酸化物粉末とを混合した後，これらを焼成することにより得られる。

【０００４】

【解決しようとする課題】ところで，上記金属化合物を電極活物質として用いた非水電解質電池用電極について，その充放電を行う場合，上記電極活物質中にリチウムイオンが出入りする。そして，これに伴い，$LiMn_2O_4$ 粉末中の多結晶体粒子３の膨張，収縮がおこる。

【０００５】そのため，前述した金属化合物の粉末９に結晶欠陥が生じる。また，結晶粒界に歪みが蓄積し，微粉化や，結晶構造の崩壊が生じる。それ故，非水電解質電池用電極の充放電寿命が短くなる。本発明はかかる従来の問題点に鑑み，充放電に伴う電極活物質の微粉化や結晶構造の崩壊を抑制し，充放電サイクル寿命の長い非水電解質電池用電極を提供しようとするものである。

【０００６】

【課題の解決手段】本発明は，リチウムを吸蔵，放出しうる金属化合物の粉末を電極活物質として用いた非水電解質電池用電極であって，上記金属化合物の粉末は多結晶体粒子の集合体からなると共に超微粉末を含有し，該超微粉末は，上記多結晶体粒子の粒子内或いは結晶粒界もしくはその両方に存在していることを特徴とする非水電解質電池用電極にある。

【０００７】本発明において最も注目すべきことは，上記超微粉末が，上記金属化合物の多結晶体粒子の粒子内或いは結晶粒界もしくはその両方に存在していることである（図１，図２参照）。ここに，超微粉末は，粒径３μｍ以下であることが好ましい。また，超微粉末の分散を均一にするために，好ましくは０．５μｍ，更に好ましくは０．２μｍ以下である。粒径が３μｍを越える場合には，超微粉末を金属化合物中に取り込むことが困難になる。超微粉末は，上記多結晶体粒子と反応しないものを用いる。このような超微粉末としては，例えばSi_3N_4，ＳｉＣ，Al_2O_3 等の粉末がある。

【０００８】上記リチウムを吸蔵又は放出しうる金属化合物としては，リチウムを含む金属化合物であることが好ましい。このような金属化合物としては，$LiMn_2O_4$，Li_xMnO_2，$LiCoO_2$，$LiNiO_2$，$LiFeO_2$，LiV_3O_8などがある。

【０００９】また，上記リチウムを吸蔵又は放出しうる他の金属化合物としては，リチウムを含まないV_2MoO_8，$Cu_2V_2O_7$，MoO_3，V_2O_5，Cr_2O_5，MnO_2，TiS_2，MoS_2 等がある。また，超微粉末は金属化合物の粉末中に０．１～４０％（容量比，以下同様）含有されていることが好ましい。０．１％未満では本発明の効果を得難く，一方，４０％を越えると副生成物を生ずるおそれがある。

【００１０】上記の超微粉末を含有する金属化合物の粉末を製造するに当たっては，例えば金属化合物の原料に上記超微粉末を添加混合し加熱焼成する方法がある。或いは，金属化合物の金属イオンを含有する溶液中に超微粉末を添加混合し沈澱を生成させた後加熱焼成する方法等がある。

【００１１】上記加熱焼成をする際には，常圧で焼成してもよいが，圧力を印加する加圧焼結法，例えばホットプレス法，熱間静水圧焼結法（ＨＩＰ）等を用いることもできる。また，加熱焼成温度は３００～１２００℃とすることが好ましい。これにより，焼結反応を促進することができる。

【００１２】上記非水電解質電池用電極は，集電体と，該集電体を被覆している電極活物質とからなる。集電体は，導電性の良い，炭素薄膜，炭素繊維，グラファイト繊維，金属，導電性高分子等を用いる。上記電極活物質は，上記金属化合物に，導電剤及び結着剤等を混練して得られる。導電剤としては，カーボン，金属等を用いる。また，結着剤としては，テフロン等を用いる。

【００１３】

【作用及び効果】本発明の非水電解質電池用電極におい

ては，電極活物質に用いる上記金属化合物の粉末中において，該金属化合物の多結晶体粒子の粒子内或いは結晶粒界もしくはその両方に，上記超微粉末が存在している。また，超微粉末は，多結晶体粒子よりも小さい。

【0014】そのため，この電極活物質を電池に組み込んで，充放電をおこなったとき，リチウムイオンの出入りに伴う多結晶体粒子の膨張，収縮は，上記超微粉末によって抑制される。即ち，上記超微粉末が，上記多結晶体粒子の膨張，収縮を和らげるクッションとしての役割を果たす。

【0015】それ故，上記多結晶体粒子の結晶構造の崩壊がなく，該多結晶体粒子の集合体である金属化合物の粉末が，微粉化することがない。したがって，上記非水電解質電池用電極のサイクル寿命が長くなる。以上のごとく本発明によれば，充放電に伴う電極活物質の微粉化や結晶構造の崩壊を抑制し，充放電サイクル寿命の長い非水電解質電池用電極を提供することができる。

【0016】

【実施例】

実施例1

本例の非水電解質電池用電極について，図1を用いて説明する。本例の非水電解質電池用電極は，リチウムを吸蔵，放出しうる金属化合物の粉末9を，電極活物質として用いた。上記金属化合物の粉末9は，多結晶体粒子3の集合体からなると共に超微粉末1を含有している。該超微粉末1は，上記多結晶体粒子3の粒子内に存在している。

【0017】上記金属化合物の粉末9を製造するに当たっては，ＬｉＩ（ヨウ化リチウム）とMnO_2（二酸化マンガン）とをＬｉ／Ｍｎ＝１／２のモル比で秤量し，混合した。この混合物にSi_3N_4超微粉末を，金属化合物中のSi_3N_4量が３ｖｏｌ％になるように添加し，混合した。上記添加した超微粉末は，上記ＬｉＩとMnO_2との混合物と反応しないものである。次いで，これをホットプレス法により，９００℃，３０ＭＰａ，N_2雰囲気中で，６０分間，加熱焼成した。これにより，金属化合物の粉末９を得た。

【0018】次に，上記金属化合物の微細構造について観察したところ，図1に示すごとく，粒径が約０．５μｍの超微粉末１が，粒径約５μｍの多結晶体粒子３の粒内に存在していることが認められた。また，上記金属化合物についてＸ線回折をしたところ，$LiMn_2O_4$の多結晶体粒子３とSi_3N_4の超微粉末１とが同定された。そして，この金属化合物の粉末９に，導電剤及び結着剤を混練して，電極活物質を作製した。導電剤としてはカーボンを用い，結着剤としてはテフロンを用いた。これを集電体の周囲に付着させて非水電解質電池用電極を作製した。

【0019】実施例２

本例においては，図２に示すごとく，金属化合物の粉末９において，多結晶体粒子３の粒子内及び結晶粒界に超微粉末１，２が存在している。上記金属化合物の粉末を製造するに当たっては，ＬｉＩとMnO_2とをＬｉ／Ｍｎ＝１／２のモル比で秤量し，混合した。この混合物にSi_3N_4超微粉末を，金属化合物中のSi_3N_4量が２０ｖｏｌ％になるように添加し，混合した。次いで，これを実施例１と同様に加熱焼成し，金属化合物の粉末９を得た。

【0020】次に，上記金属化合物の粉末９の微細構造について観察した。その結果，図２に示すごとく，多結晶体粒子３の粒子内には粒径０．５μｍの超微粉末１が存在していた。また上記多結晶体粒子３の結晶粒界には，粒径１μｍ以上の超微粉末２が存在していることが認められた。そして，実施例１と同様にして，本例にかかる金属化合物の粉末９を用いて，非水電解質電池用電極を作製した。その他は，実施例１と同様である。

【0021】実施例３

本例においては，まず$MnSO_4$水溶液中で超微粉末の周囲に二酸化マンガンを析出させた後，Li_2SO_4水溶液中で$LiMn_2O_4$を生長させて，金属化合物を得た。即ち，まず，７５ｇの$MnSO_4$を水５００ｍｌに溶解し，粒径０．５μｍのSi_3N_4超微粉末を１．５ｇ加えた。次いで，この溶液に１Ｎ－アンニモア水を徐々に攪拌しながら加え，沈澱を生成させた。

【0022】次に，溶液中に酸素を１００ｍｌ／分の流量で５時間吹き込み，酸化処理を行った。次に，沈澱を濾過，乾燥し，空気中，３００℃で１０時間熱処理を行ない二酸化マンガンを得た。次に，このようにして得られた二酸化マンガン４０ｇを４Ｎ－ＬｉＯＨ溶液５００ｍｌ中に投入し，攪拌しながら７０℃で５時間反応させ，その後濾過，乾燥を行ない，この粉末を９００℃で２４時間熱処理を行った。

【0023】得られた粉末をＸ線回折した結果，$LiMn_2O_4$の多結晶粒子とSi_3N_4の超微粉末が同定された。また，粉末の微細構造は，実施例１の金属化合物と同様であった（図１参照）。そして，実施例１と同様にして，本例にかかる金属化合物の粉末９を用いて，非水電解質電池用電極を作製した。その他は，実施例１と同様である。

【0024】実施例４

本例において，$MnSO_4$及びLi_2SO_4を溶解した水溶液中で超微粉末の周囲に$LiMn_2O_4$を析出，生長させて，金属化合物を得た。即ち，まず７５ｇの$MnSO_4$と３０ｇのLi_2SO_4とを水５００ｍｌに溶解し，粒径０．５μｍのSi_3N_4超微粉末を１．５ｇ加えた。次いで，この溶液に１Ｎ－アンモニア水を徐々に攪拌しながら加え，沈澱を生成させた。次に，この溶液中に酸素を１００ｍｌ／分の流量で５時間吹き込み，酸化処理を行った。次に沈澱を濾過，乾燥し，空気中９００℃で２４時間熱処理を行った。

【００２５】得られた粉末をＸ線回折した結果，$LiMn_2O_4$の多結晶粒子とSi_3N_4の超微粉末とが同定された。また粉末の微細構造は，実施例１の金属化合物と同様であった（図１参照）。そして，実施例１と同様にして，本例にかかる金属化合物の粉末９を用いて，非水電解質電池用電極を作製した。その他は，実施例１と同様である。

【００２６】比較例

本例においては，上記実施例１～４と異なり，超微粉末が存在しない上記金属化合物の粉末を作製した。該金属化合物は，多結晶体粒子の集合体からなる。該多結晶体粒子の粒径は約５μｍであった。そして，上記実施例１～４と同様にして，非水電解質電池用電極を作製した。その他は，実施例１～４と同様である。

【００２７】実験例

本例においては，上記実施例１～４及び比較例にかかる非水電解質電池用電極を用いて非水電解質二次電池を組み立て，各非水電解質電池用電極の充放電サイクル数に対するエネルギ容量維持率の変化を測定した。上記非水電解質二次電池は，直径２０ｍｍ，厚み３．２ｍｍのボタン型電池である。負極には，金属リチウムを用いた。電解液としては，プロピレンカーボネートに過塩素酸リチウムを溶解したものを用いた。

【００２８】上記測定に際して，上記ボタン型電池について，２ｍＡ／cm^2の定電流，上限電圧４．１Ｖの条件で，５時間充電を行ない，その後２Ｖまで放電する充放電サイクル試験を行った。その結果を図４に示す。図４より知られるごとく，実施例１～４にかかる非水電解質電池用電極は，充放電サイクル数１００回までは，エネルギ容量維持率が低下しなかった。一方，比較例にかかる非水電解質電池用電極は，充放電サイクル数が１００回目で６０％まで低下した。以上のことは，本発明の非水電解質電池用電極は，充放電に伴う電極活物質の微粉化や結晶構造の崩壊が抑制され，充放電サイクル寿命が長いものであることが示すものである。

【図面の簡単な説明】

【図１】実施例１にかかる，金属化合物の微細構造を示す説明図。

【図２】実施例２にかかる，金属化合物の微細構造を示す説明図。

【図３】従来例にかかる，金属化合物の微細構造を示す説明図。

【図４】実験例における，非水電解質電池用電極の充放電サイクル数とエネルギ容量維持率との関係を示す線図。

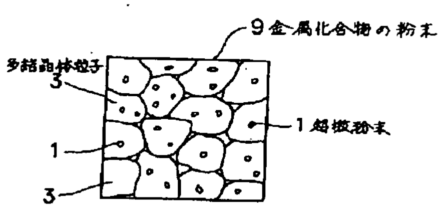
【符号の説明】

１，２．．．超微粉末，

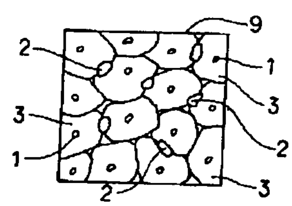
３．．．多結晶体粒子，

９．．．金属化合物の粉末，

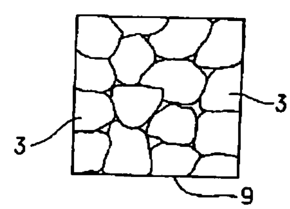
【図１】



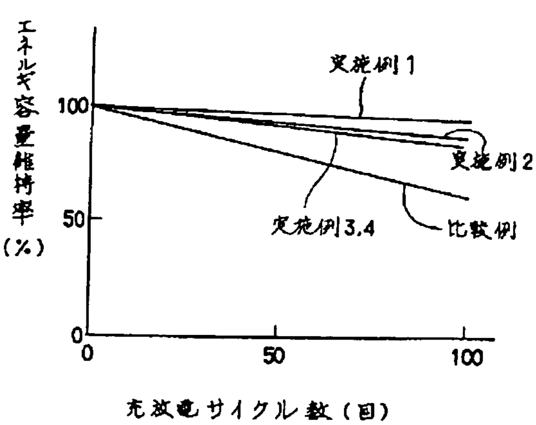
【図２】



【図３】



【図４】



CLAIMS

[Claim(s)]
[Claim 1] It is the electrode for nonaqueous electrolyte cells which is an electrode for using powder of occlusion and metallic compounds which may be emitted as electrode active material nonaqueous electrolyte [lithium] cells, and is characterized by containing the end of superfines while the powder of the above-mentioned metallic compounds consists of the aggregate of a polycrystalline-substance particle, and existing in the inside of the particle of the above-mentioned polycrystalline-substance particle, or the grain boundary or its both this end of superfines.
[Claim 2] It is the electrode for nonaqueous electrolyte cells characterized by being the metallic compounds with which occlusion and the metallic compounds which may be emitted contain a lithium for the above-mentioned lithium in a claim 1.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention suppresses the pulverization of an electrode active material and the decay of the crystal structure accompanying charge and discharge, and relates to the long electrode for nonaqueous electrolyte cells of a charge-and-discharge cycle life.
[0002]
[Description of the Prior Art] the nonaqueous electrolyte rechargeable battery which uses a lithium or a lithium alloy as an electrode -- setting -- as the electrode active material -- the former -- MnO2 and V2 O5 etc. -- metallic compounds are examined However, these metallic oxides have the remarkable reduction in energy capacity because of destruction of the crystal structure by charge and discharge. LiMn 2O4 which contained the lithium ion beforehand as the cure etc. -- using a lithium multiple oxide as metallic compounds is proposed (Material Research Bulletin 18 (1983) 461-472)
[0003] it is shown in drawing 3 -- as -- LiMn 2O4 from -- the powder 9 of the becoming metallic compounds is the aggregate of the polycrystalline-substance particle 3 This polycrystalline-substance particle 3 is the cubic crystal structure which carried out Spinel structure. Generally the particle size of the powder 9 of these metallic compounds is 10 micrometers of numbers from several micrometers. The powder of the above-mentioned metallic compounds is obtained by calcinating these, after mixing for example, lithium salt powder and manganic acid ghost powder.
[0004]
[Problem(s) to be Solved] By the way, about the electrode for nonaqueous electrolyte cells using the above-mentioned metallic compounds as an electrode active material, when performing the charge and discharge, a lithium ion goes in and out into the above-mentioned electrode active material. And it follows on this and is LiMn 2O4. Expansion of the polycrystalline-substance particle 3 in powder and contraction start.
[0005] Therefore, a crystal defect arises to the powder 9 of the metallic compounds mentioned above. Moreover, distortion is accumulated to the grain boundary and pulverization and decay of the crystal structure arise. So, the charge-and-discharge life of the electrode for nonaqueous electrolyte cells becomes short. In view of this conventional trouble, this invention tends to suppress the pulverization of an electrode active material and the decay of the crystal structure accompanying charge and discharge, and tends to offer the long electrode for nonaqueous electrolyte cells of a charge-and-discharge cycle life.
[0006]
[Means for Solving the Problem] this invention is the electrode for nonaqueous electrolyte cells which used the powder of occlusion and the metallic compounds which may be emitted for the lithium as an electrode active material, while the powder of the above-mentioned metallic compounds consists of the aggregate of a polycrystalline-substance particle, the end of superfines is contained, and it is in the electrode for nonaqueous electrolyte cells characterized by existing in the inside of the particle of the above-mentioned polycrystalline-substance particle, or the grain boundary or its both this end of superfines.
[0007] What should be most observed in this invention is that the above-mentioned end of superfines exists in the inside of the particle of the polycrystalline-substance particle of the above-mentioned metallic compounds, or the grain boundary or its both (refer to drawing 1 and drawing 2). It is desirable that it is the particle size of 3 micrometers or less the end of superfines here. Moreover, in order to make distribution in the end of superfines uniform, 0.5 micrometers is 0.2 micrometers or less still more preferably preferably. When particle size exceeds 3 micrometers, it becomes difficult to incorporate the end of superfines in metallic compounds. The above-mentioned polycrystalline-substance particle and the thing which does not react are used the end of superfines. as such end of superfines -- Si 3N4, SiC, and aluminum 2O3 etc. -- there is powder
[0008] It is desirable that they are the metallic compounds which contain a lithium for the above-mentioned lithium as occlusion or metallic compounds which may be emitted. As such metallic compounds, there are LiMn2 O4, Lix MnO2, LiCoO2, LiNiO2, LiFeO2, LiV 3O8, etc.
[0009] moreover, V2 MoO8 which does not contain a lithium for the above-mentioned lithium as occlusion or other metallic compounds which may be emitted, Cu 2V2O7, MoO3, V2 O5, Cr 2O5, MnO2, TiS2, and MoS2 etc. -- it is moreover, it is desirable that content is carried out 0.1 to 40% (a capacity factor and the following -- the same) into the powder of metallic compounds the end of superfines At less than 0.1%, it is a book.
[0010] In manufacturing the powder of the metallic compounds containing the above-mentioned end of superfines, addition mixture of the above-mentioned end of superfines is carried out, and the method of carrying out heating baking is, for example in

the raw material of metallic compounds. Or there is the method of carrying out afterbaking baking of having carried out addition mixture of the end of superfines into the solution containing the metal ion of metallic compounds, and having made sedimentation generating etc.

[0011] Although you may calcinate by the ordinary pressure in case the above-mentioned heating baking is carried out, the pressure-sintering method for impressing a pressure, for example, hot pressing, hot isostatic pressing (HIP), etc. can also be used. Moreover, as for heating burning temperature, it is desirable to consider as 300-1200 degrees C. Thereby, a sintering reaction can be promoted.

[0012] The above-mentioned electrode for nonaqueous electrolyte cells consists of a charge collector and an electrode active material which has covered this charge collector. A carbon thin film with sufficient conductivity, a carbon fiber, a graphite fiber, a metal, a conductive polymer, etc. are used for a charge collector. The above-mentioned electrode active material kneads an electric conduction agent, a binder, etc. to the above-mentioned metallic compounds, and is obtained. Carbon, a metal, etc. are used as an electric conduction agent. Moreover, Teflon etc. is used as a binder.

[0013]

[Function and Effect] In the electrode for nonaqueous electrolyte cells of this invention, the above-mentioned end of superfines exists at the inside of the particle of the polycrystalline-substance particle of these metallic compounds, or the grain boundary or its both in the powder of the above-mentioned metallic compounds used for an electrode active material. Moreover, it is smaller than a polycrystalline-substance particle the end of superfines.

[0014] Therefore, when this electrode active material is included in a cell and charge and discharge are performed, expansion of the polycrystalline-substance particle accompanying receipts and payments of a lithium ion and contraction are suppressed by the above-mentioned end of superfines. That is, the above-mentioned end of superfines plays a role of a cushion which softens expansion of the above-mentioned polycrystalline-substance particle and contraction.

[0015] So, there is no decay of the crystal structure of the above-mentioned polycrystalline-substance particle, and the powder of the metallic compounds which are the aggregate of this polycrystalline-substance particle does not carry out pulverization. Therefore, the cycle life of the above-mentioned electrode for nonaqueous electrolyte cells becomes long. Like the above, according to this invention, the pulverization of an electrode active material and the decay of the crystal structure accompanying charge and discharge can be suppressed, and the long electrode for nonaqueous electrolyte cells of a charge-and-discharge cycle life can be offered.

[0016]

[Example]

The electrode for nonaqueous electrolyte cells of the example of one example is explained using drawing 1 . The powder 9 of occlusion and the metallic compounds which may be emitted was used for the electrode for nonaqueous electrolyte cells of this example for the lithium as an electrode active material. The powder 9 of the above-mentioned metallic compounds contains 1 in the end of superfines while consisting of the aggregate of the polycrystalline-substance particle 3. 1 exists in the particle of the above-mentioned polycrystalline-substance particle 3 in this end of superfines.

[0017] In manufacturing the powder 9 of the above-mentioned metallic compounds, weighing capacity of LiI (iodation lithium) and MnO2 (manganese dioxide) was carried out by the mole ratio of Li/Mn=1/2, and it mixed. It is Si 3N4 to this mixture. About the end of superfines, it is Si 3N4 in metallic compounds. It added so that an amount might become 3vol(s)%, and it mixed. They are the above LiI and MnO2 the end of superfines addition was carried out [above-mentioned]. It does not react with mixture. Subsequently, it is this by hot pressing 900 degrees C, 30MPa, and N2 In atmosphere, heating baking was carried out for 60 minutes. This obtained the powder 9 of metallic compounds.

[0018] Next, when observed about the fine structure of the above-mentioned metallic compounds, as shown in drawing 1 , it was admitted that 1 existed in the end of superfines whose particle size is about 0.5 micrometers in the grain with a particle size of about 5 micrometers of the polycrystalline-substance particle 3. Moreover, when the X diffraction was carried out about the above-mentioned metallic compounds, it is LiMn 2O4. The polycrystalline-substance particle 3 and Si 3N4 1 was identified in the end of superfines. And the electric conduction agent and the binder were kneaded to the powder 9 of these metallic compounds, and the electrode active material was produced to it. Teflon was used as a binder, using carbon as an electric conduction agent. This was made to adhere to the circumference of a charge collector, and the electrode for nonaqueous electrolyte cells was produced.

[0019] In the example of two examples, as shown in drawing 2 , in the powder 9 of metallic compounds, 1 and 2 exist in the inside of the particle of the polycrystalline-substance particle 3, and the grain boundary in the end of superfines. If in charge of manufacturing the powder of the above-mentioned metallic compounds, it is LiI and MnO2. By the mole ratio of Li/Mn=1/2, weighing capacity was carried out and it mixed. It is Si 3N4 to this mixture. About the end of superfines, it is Si 3N4 in metallic compounds. It added so that an amount might become 20vol(s)%, and it mixed. Subsequently, heating baking of this was carried out like the example 1, and the powder 9 of metallic compounds was obtained.

[0020] Next, it observed about the fine structure of the powder 9 of the above-mentioned metallic compounds. Consequently, as shown in drawing 2 , 1 existed in the particle of the polycrystalline-substance particle 3 in the superfines end of 0.5-micrometer particle size. Moreover, it was accepted in the grain boundary of the above-mentioned polycrystalline-substance particle 3 that 2 exists in the superfines end of particle size 1 micrometers or more. And the electrode for nonaqueous electrolyte cells was produced like the example 1 using the powder 9 of the metallic compounds concerning this example. Others are the same as that of an example 1.

[0021] It sets for the example of three examples, and is MnSO4 first. Li2 SO4 after depositing manganese dioxide to the circumference in the end of superfines in solution It is LiMn 2O4 in solution. It was made to grow and metallic compounds were obtained. That is, it is 75g MnSO4 first. It dissolves in 500ml of water, and is Si 3N4 with a particle size of 0.5 micrometers. The superfines end of 1.5g was added. Subsequently, sedimentation was made to generate in addition, stirring 1N-ANNIMOA water gradually in this solution.
[0022] Next, oxygen was blown by 100ml flow rate for /into the solution for 5 hours, and oxidation treatment was performed. Next, sedimentation was filtered and it dried, and among air, heat treatment was performed at 300 degrees C for 10 hours, and manganese dioxide was obtained. Next, it was made to react at 70 degrees C for 5 hours, having supplied 40g of manganese dioxide obtained by doing in this way in 500ml of 4 N-LiOH solutions, and stirring it, filtration and dryness were performed after that, and heat treatment was performed for this powder at 900 degrees C for 24 hours.
[0023] As a result of carrying out the X diffraction of the obtained powder, it is LiMn 2O4. The superfines end of a polycrystal particle and Si 3N4 was identified. Moreover, the powdered fine structure was the same as that of the metallic compounds of an example 1 (refer to drawing 1). And the electrode for nonaqueous electrolyte cells was produced like the example 1 using the powder 9 of the metallic compounds concerning this example. Others are the same as that of an example 1.
[0024] It sets for the example of four examples, and is MnSO4. And Li2 SO4 It is LiMn 2O4 to the circumference in the end of superfines in the solution which dissolved. It was made to deposit and grow and metallic compounds were obtained. That is, it is 75g MnSO4 first. 30g Li2 SO4 It dissolves in 500ml of water, and is Si 3N4 with a particle size of 0.5 micrometers. The superfines end of 1.5g was added. Subsequently, sedimentation was made to generate in addition, stirring 1N-aqueous ammonia gradually in this solution. Next, oxygen was blown by 100ml flow rate for /into this solution for 5 hours, and oxidation treatment was performed. Next, sedimentation was filtered, it dried and heat treatment was performed at 900 degrees C among air for 24 hours.
[0025] As a result of carrying out the X diffraction of the obtained powder, it is LiMn 2O4. A polycrystal particle and the superfines end of Si 3N4 were identified. Moreover, the powdered fine structure was the same as that of the metallic compounds of an example 1 (refer to drawing 1). And the electrode for nonaqueous electrolyte cells was produced like the example 1 using the powder 9 of the metallic compounds concerning this example. Others are the same as that of an example 1.
[0026] Unlike the above-mentioned examples 1-4, in the example of the example book of comparison, the powder of the above-mentioned metallic compounds with which the end of superfines does not exist was produced. These metallic compounds consist of the aggregate of a polycrystalline-substance particle. The particle size of this polycrystalline-substance particle was about 5 micrometers. And the electrode for nonaqueous electrolyte cells was produced like the above-mentioned examples 1-4. Others are the same as that of examples 1-4.
[0027] In the example of the example book of an experiment, the nonaqueous electrolyte rechargeable battery was assembled using the electrode for nonaqueous electrolyte cells concerning the above-mentioned examples 1-4 and the example of comparison, and change of the energy capacity maintenance factor to the number of charge-and-discharge cycles of each electrode for nonaqueous electrolyte cells was measured. The above-mentioned nonaqueous electrolyte rechargeable battery is a button type cell with a diameter [of 20mm], and a thickness of 3.2mm. The metal lithium was used for the negative electrode. As the electrolytic solution, what dissolved the lithium perchlorate in propylene carbonate was used.
[0028] The above-mentioned measurement is faced and it is 2 mA/cm2 about the above-mentioned button type cell. On condition that a constant current and upper limit voltage 4.1V, charge was performed for 5 hours and the charge-and-discharge cycle examination which discharges to after that 2V was performed. The result is shown in drawing 4 . As for the electrode for nonaqueous electrolyte cells concerning examples 1-4, an energy capacity maintenance factor did not fall to 100 charge-and-discharge cycle numbers so that it might be known from drawing 4 . On the other hand, as for the electrode for nonaqueous electrolyte cells concerning the example of comparison, the number of charge-and-discharge cycles fell to 60% by the 100th time. The pulverization of an electrode active material and the decay of the crystal structure accompanying [thing / above] charge and discharge in the electrode for nonaqueous electrolyte cells of this invention are suppressed, and that a charge-and-discharge cycle life is long shows.

[Translation done.]